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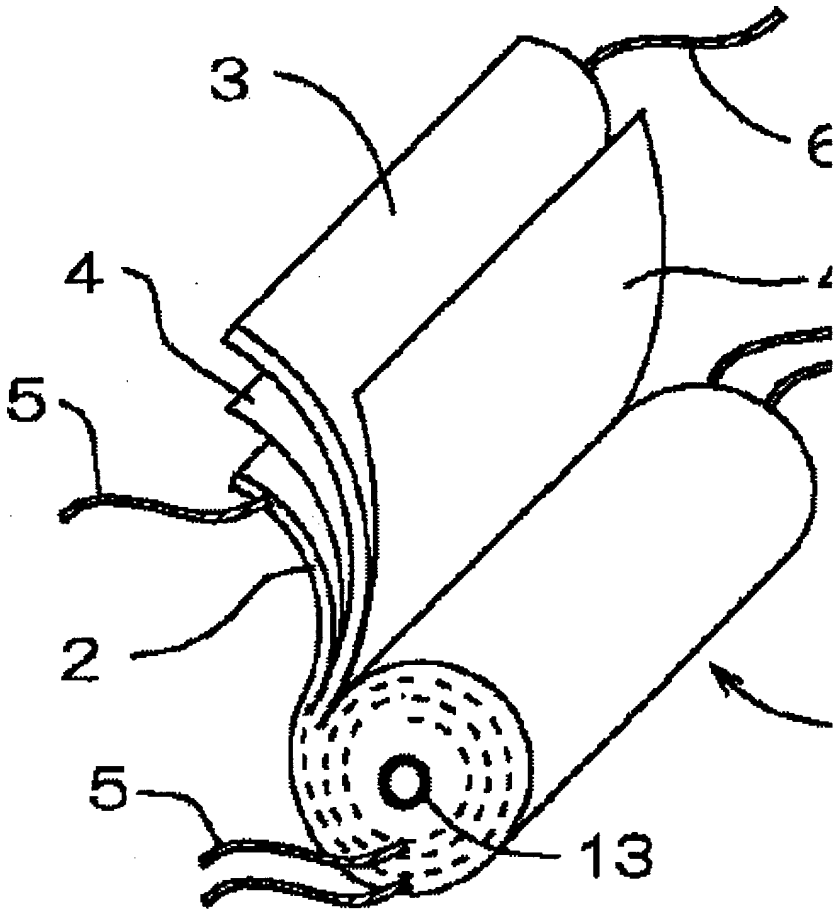
(54) LITHIUM SECONDARY BATTERY

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a secondary battery that restrains degradation of nonaqueous electrolyte by suppressing the effect of HF in the nonaqueous electrolyte and improves cycle characteristics.

SOLUTION: The lithium secondary battery is equipped with an electrode body 1, which is wound or laminated with a positive electrode plate 2 and a negative electrode plate 3 having a separator in-between, and uses a nonaqueous electrolyte containing lithium compound as an electrolyte. Three dimensional siloxane compound is contained in one of the positive electrode plate 2, negative electrode plate 3, separator 4 or the nonaqueous electrolyte.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(57)【要約】
【課題】非水液電解液中のHFの影響を抑えることで、非水電解液の劣化を抑制し、サイクル特性を改善したリチウム二次電池を提供する。
【解決手段】正極板2と負極板3をセパレータ4を介して、捲回若しくは積層してなる電極体1を備え、リチウム化合物を電解質として含む非水電解液を用いたリチウム二次電池である。正極板2、負極板3、セパレータ4、非水電解液の少なくともいずれかに、3次元型シロキサン化合物を含ませた。

【特許請求の範囲】
【請求項1】正極板と負極板をセパレータを介して、捲回若しくは積層してなる電極体を備え、リチウム化合物を電解質として含む非水電解液を用いたリチウム二次電池であって、当該正極板、当該負極板、当該セパレータ、及び当該非水電解液の少なくともいずれかに、3次元型シロキサン化合物が含まれていることを特徴とするリチウム二次電池。
【請求項2】電池容量が2Ah以上であることを特徴とする請求項1に記載のリチウム二次電池。
【請求項3】車載用電池であることを特徴とする請求項1又は2に記載のリチウム二次電池。
【請求項4】電気自動車又はハイブリッド電気自動車に用いられることを特徴とする請求項3に記載のリチウム二次電池。
【請求項5】エンジン起動用に用いられることを特徴とする請求項3に記載のリチウム二次電池。

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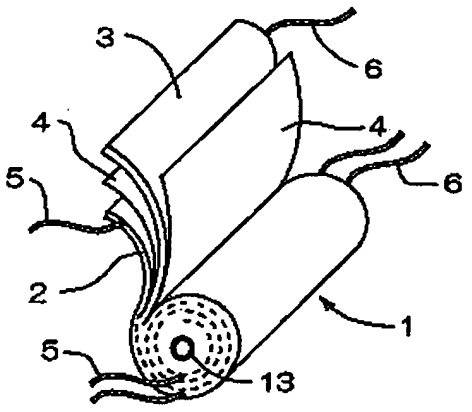
最終頁に続く

(54)【発明の名称】　リチウム二次電池

(57)【要約】
【課題】　非水液電解液中のＨＦの影響を抑えることで、非水電解液の劣化を抑制し、サイクル特性を改善したリチウム二次電池を提供する。
【解決手段】　正極板２と負極板３をセパレータ４を介して、捲回若しくは積層してなる電極体１を備え、リチウム化合物を電解質として含む非水電解液を用いたリチウム二次電池である。正極板２、負極板３、セパレータ４、非水電解液の少なくともいずれかに、３次元型シロキサン化合物を含ませた。



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【特許請求の範囲】

【請求項１】 正極板と負極板をセパレータを介して、捲回若しくは積層してなる電極体を備え、リチウム化合物を電解質として含む非水電解液を用いたリチウム二次電池であって、

当該正極板、当該負極板、当該セパレータ、及び当該非水電解液の少なくともいずれかに、

３次元型シロキサン化合物が含まれていることを特徴とするリチウム二次電池。

【請求項２】 電池容量が２Ａｈ以上であることを特徴とする請求項１に記載のリチウム二次電池。

【請求項３】 車載用電池であることを特徴とする請求項１又は２に記載のリチウム二次電池。

【請求項４】 電気自動車又はハイブリッド電気自動車に用いられることを特徴とする請求項３に記載のリチウム二次電池。

【請求項５】 エンジン起動用に用いられることを特徴とする請求項３に記載のリチウム二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】 本発明は、サイクル特性及び信頼性に優れたリチウム二次電池に関する。

【０００２】

【従来の技術】 リチウム二次電池は、近年、携帯型の通信機器やノート型パーソナルコンピュータ等の電子機器の電源を担う、小型でエネルギー密度の大きな充放電可能な二次電池として、広く用いられるようになってきている。また、国際的な地球環境の保護を背景として省資源化や省エネルギー化に対する関心が高まる中、リチウム二次電池は、自動車業界においては電気自動車やハイブリッド電気自動車用のモータ駆動用バッテリーとして、また、電力業界においては夜間電力の保存による電力の有効利用手段として、それぞれ期待されており、これらの用途に適する大容量リチウム二次電池の実用化が急務とされている。

【０００３】 リチウム二次電池には、一般的に、正極活物質としてリチウム遷移金属複合酸化物等が、負極活物質としてハードカーボンや黒鉛といった炭素質材料がそれぞれ用いられる。また、このような材料を用いたリチウム二次電池の反応電位は約４．１Ｖと高く、このため非水電解液として、従来の二次電池のような水系非水電解液を用いることができない。そこで、リチウム二次電池の非水電解液としては、有機溶媒にリチウムイオン（Ｌｉ＋）電解質たるリチウム化合物を溶解した非水電解液が用いられる。

【０００４】

【発明が解決しようとする課題】 ここで、非水電解液の原料となる有機溶媒には、製造段階からコンタミとして微量であるが水分が混在していることが常である。また、電池を構成する各種の材料や部品、例えば、電極活物質粉末や集電基板（金属箔）、金属端子、電池ケース等は、一般的には通常の大気雰囲気において保存されるため、それら材料や部品の表面に吸着していた水分が、電池を作成し終えた時点で、非水電解液に入り込むことがあり得る。

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【０００５】 このような水分が非水電解液中に存在していると、水分により電解質が分解し、酸性物質やガス等が発生する危険性が高くなり、結果的に充放電サイクル特性（充放電の繰り返しによる電池容量変化特性を指す。以下、「サイクル特性」という。）が劣化し、電池寿命が短くなる問題が生ずる。

【０００６】 例えば、六フッ化リン酸リチウム（Ｌｉ＋ＰＦ６－）は、有機溶媒に溶解して高い電導度を示すために、電解質として最も注目されているが、Ｌｉ＋ＰＦ６－を用いた場合には、有機溶媒中に水分が存在するとフッ化水素酸（ＨＦ）が発生する。このＨＦは電池容器や集電体の金属材料を溶解・腐食させ、また、正極活物質を溶解して遷移金属を溶出させる。更に負極活物質表面に金属を含んだ悪質なＳＥＩ（Ｓｏｌｉｄ Ｅｌｅｃｔｒｏｌｙｔｅ Ｉｎｔｅｒｆａｃｅ）層を形成してＬｉ＋の作用を阻害する等して、電池劣化の原因となることが知られている。この様な電池特性の劣化は、充放電を繰り返すサイクル運転において顕著に現れ、二次電池の致命的欠陥となる。

【０００７】 そこで、特開平８－７８０５３号公報には、非水電解液中に、分子構造内に、（－Ｓｉ－Ｏ－Ｓｉ－）のシリコーン骨格を含んだ、１次元構造である直鎖状ポリシロキサン化合物を添加することで、電流特性を向上させ、サイクル特性の向上が図られる旨開示している。しかし、この方法では、添加物が直鎖状のものであることから、電解液中において不安定であり、また、高分子であることから、その物性にはばらつきがでることになる。しかも、この添加物を含ませたリチウム二次電池は、その充放電を繰り返す使用時において、電池自体が高温になった場合には、低分子量のものから分子鎖が切れてしまうので、添加剤としての効果は失われ、逆に電池反応の阻害物となる。従って、高出力性及び長期サイクル特性において高性能を必要とする電気自動車等の用途には全く適さない。

【０００８】

【課題を解決するための手段】 本発明は上述した従来技術の問題点に鑑みてなされたものであり、その目的とするところは、電解液や電池部材等に含まれている水分を発生原因物質として、結果的に電極体や非水電解液に含まれることとなるＨＦを不活性化することにより、電池反応の阻害を抑制して、サイクル特性及び信頼性に優れたリチウム二次電池を提供することにある。

【０００９】 即ち、本発明によれば、正極板と負極板をセパレータを介して、捲回若しくは積層してなる電極体を備え、リチウム化合物を電解質として含む非水電解

液を用いたリチウム二次電池であって．当該正極板、当該負極板、当該セパレータ．及び当該非水電解液の少なくともいずれかに、３次元型シロキサン化合物が含まれていることを特徴とするリチウム二次電池、が提供される。

【００１０】　本発明のリチウム二次電池においては、後述する化合物に導電助剤となるアセチレンブラック等の電子伝導性粒子が分散されていることも好ましい。このような当該化合物は、電池反応に寄与することなく、しかも導電助剤を添加することにより内部抵抗の上昇は抑えられ、良好なＨＦの反応抑制剤となる。

【００１１】　本発明のリチウム二次電池は、電池容量が２Ａｈ以上の大型電池に好適に採用される。また、車載用電池として好適に採用され、高出力を必要とするエンジン起動用電源、大電流の放電が頻繁に行われる電気自動車又はハイブリッド電気自動車のモータ駆動用電源等として好適に用いられる。

【００１２】

【発明の実施の形態】　本発明のリチウム二次電池は、溶解してリチウムイオン（Ｌｉ＋）を生ずるリチウム化合物を電解質として含む非水電解液を用いたものであって．その非水電解液の劣化による電池反応の阻害を抑制することによりサイクル特性の向上を図ったものである。以下、本発明の実施形態について説明するが．本発明が以下の実施形態に限定されないことはいうまでもない。

【００１３】　本発明のリチウム二次電池は、正極板２．負極板３．セパレータ４及び非水電解液の少なくともいずれかに．３次元型シロキサン化合物が含まれるようにする。ここで、「当該化合物が含まれる」とは、当該化合物の添加された非水電解液が．電極板２・３やセパレータ４に含浸されることにより．当該化合物が電極板２・３やセパレータ４に含まれることとなる場合や、電極板２・３やセパレータ４に予め塗布された当該化合物が．非水電解液を充填した際に非水電解液中に移動して非水電解液にも含まれることとなる場合を含むものである。

【００１４】　本発明のリチウム二次電池においては、この化合物を含める方法として、（１）正極板．及び／又は．負極板を構成する電極活物質粒子の表面に分散、または被覆されている、（２）セパレータ表面に分散されている、（３）微細粉末化して非水電解液中に懸濁分散されている．の少なくともいずれかの方法を用いることができる。従って、これらの手段を複数併用することも．また、可能である。

【００１５】　具体的には．電極板２・３に当該化合物を含ませる方法としては．電極板２・３を、可溶な溶剤に溶かした当該化合物溶剤に浸漬する方法（ディッピング）や、スプレーや刷毛塗り等の方法を用いて電極板２・３に当該化合物を塗布する方法を挙げることができ、

いずれの場合であっても．当該化合物を含ませて後に乾燥し．その後の電極体の作製に供する。セパレータ４表面に分散、あるいは固着させるにも．同様の方法を用いることができ．また、電解液については、当該化合物を重力沈降しない程度にまで微細粉末化して均一に当該化合物を含ませることも可能である。

【００１６】　ここで、非水電解液として、予め当該化合物を添加したものを用いる方法が最も好適に採用される。この場合には、電池の組立作業工程も当該化合物の添加混合工程が増えるのみであって作業も容易であるといった利点がある。

【００１７】　すなわち．電池内に充填する電解液として．後述する電解質を所定の有機溶媒に溶解してなる一般的な非水電解液に、更に．ＨＦトラップ剤として、当該化合物を添加したものを用いる。当該化合物の添加により．内部電極体を電池へ挿入する前には非水電解液中の水分から発生したＨＦ濃度を低下させることが可能である。また、内部電極体を電池へ挿入した後においては．電極板等に吸着していた水分から発生したＨＦの除去が容易に行われることとなる。このことにより．ＨＦによる金属腐食等の抑制及び悪質なＳＥＩ生成の抑制にも寄与し、サイクル特性の向上が図られると考えられる。

【００１８】　さて、本発明に用いることができる３次元型シロキサン化合物としては、具体的には、１－アリル－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン．１－（３－クロロプロピル）－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン．１－（４－ビニルフェニル）－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン．エチル－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン－１－ウンデカノエイト．１，３，５，７，９，１１，１４－ヘプタシクロヘキシトリシクロ［７．３．３．１５，１１］ヘプタシロキサン－３，７，１４－トリオール．１，３，５，７，９，１１，１３－ヘプタシクロペンチル－１５－［２－（ジフェニルフォスフィノ）エチル］ペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン．１，３，５，７，９，１１，１３－ヘプタシクロペンチル－１５－グリシジルペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン．３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．１３，９．１５，１３．１７，１３］オクタシロキサン－１－プチロニトリル、３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．

$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン－１－オール．３－（３．５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン－１－イル）プロピルメタクリレート．１，３，５，７，９，１１，１４－ヘプタシクロペンチルトリシクロ［７．３．３．$1^{5,11}$］ヘプタシロキサン－エンド－３，７，１４－トリオール．１，３，５，７，９，１１，１３－ヘプタシクロペンチル－１５－ビニルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン．１－ヒドリド－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン．メチル－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン－１－プロピオネート．１－［２－（５－ノルボルネン－２－イル）エチル］－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン．１，３，５，７，９，１１，１３，１５－オクタキス（ジメチルシリロキシ）ペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン．１，３，５，７，９，１１，１３，１５－オクタビニルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサンが好適である。これは環状構造を有していることから電解液に安定であり，かつ高いＬｉ＋導電性を示すものであり，当該化合物として好適に用いられる。

【００１９】　ここで、本発明において、３次元型シロキサン化合物がＨＦを不活性化する機構を説明する。本発明における電解液は、水分を含まない非水電解液を用いているが、電池を組み立てた際、電池部材等に付着している水分を完全に取り除くことができないために、その電解液中には水分が微量ながら存在することとなる。そして、その水分により電解液が分解し、電解液及び電解質が分解し．ＨＦやガス（CO_2）等が発生する。

【００２０】　このとき発生したＨＦは、電池容器や集電体の金属材料を溶解・腐食させるとともに、正極活物質を溶解して遷移金属を溶出させ、金属原子を含んだ悪質なＳＥＩ生成を誘導する。なお、電解質の水による分解は．電池が高温であるほど反応は促進され、その分解は進むことになる。ＳＥＩの生成反応は発熱反応であることから、この熱により電解質の水による分解が促進され．更にＨＦが生成されることになる。

【００２１】　そこで、本発明においては、当該化合物において、ルイス塩基性を示す原子．すなわち．非共有電子対を有し電子供与性を示すＯ原子が、空の電子軌道を有するＨＦと配位的に結合してＨＦを当該化合物の分子構造内に固定化する。これにより．電池内のＨＦは不活性化され、ＨＦによる影響を抑制することが可能となる。このことにより、電池が充放電を繰り返す中．電池

自体が高温になった場合でも、当該化合物がＨＦを固定化していることにより、悪質なＳＥＩの生成が抑制される。

【００２２】　特に、本発明における化合物は．３次元構造をもち、かつ高分子量であること及び多くの環状構造を有していることから．高温においても電解液中において安定的に存在することができる。また、分子構造的に単位体積当たりのＯ原子の数が多いことから．効率的にＨＦを捕獲・固定することができる。しかも．当該化合物が有する５員環構造は．Ｌｉ＋のイオン半径よりもかなり大きく．その移動を阻害することはない。よって．本発明における３次元シロキサン化合物は．リチウム二次電池におけるサイクル特性向上の添加剤として確実に効果を発揮することになる。

【００２３】　本発明において、当該化合物には．アセチレンブラック等の電子伝導性粒子が分散されていてもよい。このことにより、電導度を上げ．内部抵抗の上昇を防ぐことができる。

【００２４】　本発明のリチウム二次電池は、溶解してリチウムイオン（Ｌｉ＋）を生ずるリチウム化合物を電解質として用いた非水電解液を用いたものである。従って．その他の材料や電池構造には何ら制限はない。以下．電池を構成する主要部材並びにその構造について概説する。

【００２５】　リチウム二次電池の心臓部とも言える電極体の一つの構造は、小容量のコイン電池にみられるような．正負各電極活物質を円板状にプレス成型したセパレータを挟んだ単セル構造である。

【００２６】　コイン電池のような小容量電池に対して．容量の大きい電池に用いられる電極体の１つの構造は捲回型である。図１の斜視図に示されるように．捲回型電極体１は．正極板２と負極板３とを、多孔性ポリマーからなるセパレータ４を介して正極板２と負極板３とが直接に接触しないように巻芯１３の外周に捲回して構成される。正極板２及び負極板３（以下、「電極板２・３」と記す。）に取り付けられている電極リード５・６の数は最低１本あればよく．複数の電極リード５・６を設けて集電抵抗を小さくすることもできる。

【００２７】　電極体の別の構造としては、コイン電池に用いられる単セル型の電極体を複数段に積層してなる積層型が挙げられる。図２に示すように、積層型電極体７は．所定形状の正極板８と負極板９とをセパレータ１０を挟み交互に積層したもので、１枚の電極板８・９に少なくとも１本の電極リード１１・１２を取り付ける。電極板８・９の使用材料や作成方法等は、捲回型電極体１における電極板２・３等と同様である。

【００２８】　次に、捲回型電極体１を例に、その構成について更に詳細に説明する。正極板２は集電芸板の両面に正極活物質を塗工することによって作製される。集電芸板としては．アルミニウム箔やチタン箔等の正極電

気化学反応に対する耐蝕性が良好である金属箔が用いられるが、箔以外にパンチングメタル或いはメッシュ（網）を用いることもできる。また、正極活物質としては、マンガン酸リチウム（$LiMn_2O_4$）やコバルト酸リチウム（$LiCoO_2$）、ニッケル酸リチウム（$LiNiO_2$）等のリチウム遷移金属複合酸化物が好適に用いられ、好ましくは、これらにアセチレンブラック等の炭素微粉末が導電助剤として加えられる。

【００２９】　正極活物質の塗工は、正極活物質粉末に溶剤や結着剤等を添加して作成したスラリー或いはペーストを、ロールコータ法等を用いて、集電基板に塗布・乾燥することで行われ、その後に必要に応じてプレス処理等が施される。

【００３０】　負極板３は、正極板２と同様にして作成することができる。負極板３の集電基板としては、銅箔若しくはニッケル箔等の負極電気化学反応に対する耐蝕性が良好な金属箔が好適に用いられる。負極活物質としては、ソフトカーボンやハードカーボンといったアモルファス系炭素質材料や人造黒鉛や天然黒鉛等の高黒鉛化炭素質粉末が用いられる。

【００３１】　セパレータ４としては、マイクロポアを有するLi^+透過性のポリエチレンフィルム（ＰＥフィルム）を、多孔性のLi^+透過性のポリプロピレンフィルム（ＰＰフィルム）で挟んだ三層構造としたものが好適に用いられる。これは、電極体の温度が上昇した場合に、ＰＥフィルムが約１３０℃で軟化してマイクロポアが潰れ、Li^+の移動即ち電池反応を抑制する安全機構を兼ねたものである。そして、このＰＥフィルムをより軟化温度の高いＰＰフィルムで挟持することによって、ＰＥフィルムが軟化した場合においても、ＰＰフィルムが形状を保持して正極板２と負極板３の接触・短絡を防止し、電池反応の確実な抑制と安全性の確保が可能となる。

【００３２】　この電極板２・３とセパレータ４の捲回作業時に、電極板２・３において電極活物質の塗工されていない集電基板が露出した部分に、電極リード５・６がそれぞれ取り付けられる。電極リード５・６としては、それぞれの電極板２・３の集電基板と同じ材質からなる箔状のものが好適に用いられる。電極リード５・６の電極板２・３への取り付けは、超音波溶接やスポット溶接等を用いて行うことができる。このとき、図１に示されるように、電極体１の一端面に一方の電極の電極リードが配置されるように電極リード５・６をそれぞれ取り付けると、電極リード５・６間の接触を防止することができ、好ましい。

【００３３】　電池の組立に当たっては、先ず、電流を外部に取り出すための端子との電極リード５・６との導通を確保しつつ、作製された電極体１を電池ケースに挿入して安定な位置にホールドする。その後、非水電解液を含浸させた後に、電池ケースを封止することで電池が作製される。

【００３４】　次に、本発明のリチウム二次電池に用いられる非水電解液について説明する。溶媒としては、エチレンカーボネート（ＥＣ）、ジエチルカーボネート（ＤＥＣ）、ジメチルカーボネート（ＤＭＣ）、プロピレンカーボネート（ＰＣ）といった炭酸エステル系のものや、γ－ブチロラクチン、テトラヒドロフラン、アセトニトリル等の単独溶媒若しくは混合溶媒が好適に用いられる。

【００３５】　このような溶媒に溶解されるリチウム化合物、即ち電解質としては、六フッ化リン酸リチウム（$LiPF_6$）やホウフッ化リチウム（$LiBF_4$）等のリチウム錯体フッ素化合物、或いは過塩素酸リチウム（$LiClO_4$）といったリチウムハロゲン化物が挙げられ、１種類若しくは２種類以上を前記溶媒に溶解して用いる。特に、酸化分解が起こり難く、非水電解液の導電性の高い$LiPF_6$を用いることが好ましい。

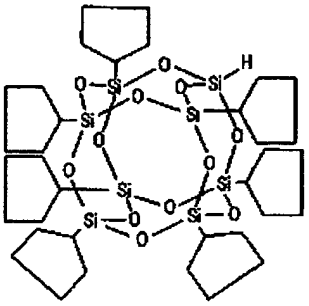
【００３６】

【実施例】　以下、本発明を実施例に基づいて、更に詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

（実施例１、比較例１）実施例１及び比較例１に係る電池は、$LiMn_2O_4$スピネルを正極活物質とし、これに導電助剤としてアセチレンブラックを外比で４重量%ほど添加したものに、更に溶剤、バインダを加えて作製した正極剤スラリーを、厚さ２０μｍのアルミニウム箔の両面にそれぞれ約１００μｍの厚みとなるように塗工して作成した正極板２と、これと同様の方法に加え、カーボン粉末を負極活物質として、厚さ１０μｍの銅箔の両面にそれぞれ約８０μｍの厚みとなるように塗工して作成した負極板３とを用いて捲回型電極体を作製し、電池ケースに収容後、非水電解液を充填して作製したものである。ここで、非水電解液としては、ＥＣとＤＥＣの等容量混合溶媒に電解質としての$LiPF_6$を１ｍｏｌ／ｌの濃度となるように溶解した溶液に、下記化学式（Ｉ）で表される当該化合物である、１－ヒドリド－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．$1^{3,9}$．$1^{5,15}$．$1^{7,13}$］オクタシロキサン、を外比で、０．１質量%ほど添加したものを用いた。これら各種電池の初回充電後の電池容量は、全て約１０Ａｈであった。

【００３７】

【化１】



(I)

【００３８】 また、サイクル試験は、図３に示される充放電サイクルを１サイクルとして、これを繰り返すことにより行った。即ち、１サイクルは放電深度５０％の充電状態の電池を１０Ｃ（放電レート）相当の電流１００Ａにて９秒間放電した後１８秒間休止し、その後７０Ａで６秒間充電後、続いて１８Ａで２７秒間充電し、再び５０％の充電状態とするパターンに設定した。なお、充電の２回目（１８Ａ）の電流値を微調整することにより、各サイクルにおける放電深度のずれを最小限に止めた。また、この耐久試験中の電池容量の変化を知るために、適宜、０．２Ｃの電流値さで充電停止電圧４．１Ｖ、放電停止電圧２．５Ｖとした容量測定を行い、所定のサイクル数における電池容量を初回の電池容量で除した値により相対放電容量を求めた。

【００３９】（評価）図４から分かるように、本発明に係る実施例１の電池は、２００００回のサイクル試験において、８２％の容量保持率を達成し、当該化合物が用いられていない比較例１よりも良好なサイクル特性を発揮した。これは、ルイス塩基性を示す原子を含んだ当該化合物が、電解液中のＨＦを不活性化した結果、サイクル寿命が向上したものと考えられる。

【００４０】 ここで、実施例１及び比較例１に係る電池は、上記の方法により、電池ケース内に当該化合物を含ませて調整した種々の電池構成部材を用いて作製した。また、その他の部材、試験環境はすべての試料について同じとし、電池部材の乾燥は電池の組立直前まで十分に行い、電池の封止不良等による電池外部からの水分の浸入等の影響も排除した。

【００４１】（実施例２、比較例２）実施例２及び比較例２にかかる電池は、$LiMn_2O_4$スピネルを正極活物質とし、これに導電助剤たるアセチレンブラックとバインダたるポリフッ化ビニリデンを重量比で、５０：２：３の比で混合したものを正極材料とし、その正極材料０．０２ｇを３００ｋｇ／ｃｍ²の圧力で直径２０ｍｍφの円板状にプレス成形して作製した正極板と、カーボンを負極板として用いてコインセル型電極体を作製し、電池ケースに収容後、非水電解液を充填して作製したものである。ここで、非水電解液としては、ＥＣとＤＥＣの等容量混合溶媒に、電池特性劣化の原因となる水分（H_2O）を１０００ｐｐｍ程添加し、また、実施例１と同じ化合物である、１－ヒドリド－３，５，７，９，１１，１３，１５－ヘプタシクロペンチルペンタシクロ［９．５．１．１³·⁹．１⁵·¹³．１⁷·¹¹］オクタシロキサン、を、５００ｐｐｍ程添加し、電解質としてＬｉＰＦ₆を１ｍｏｌ／ｌの濃度となるように溶解した溶液を用いた。これら各種電池の初回充電後の電池容量は、全て約１．３ｍＡであった。

【００４２】 次に、コインセル型電池におけるサイクル試験について説明する。本発明においては、作製したコインセルを、正極活物質の容量に応じて、１Ｃ相当の電流１．３ｍＡで電圧４．１Ｖになるまで充電後、続いて一定電圧でトータル３時間の充電を行い、同じく１Ｃ相当の電流１．３ｍＡの一定電流にて放電し、電圧が２．５Ｖになるまで放電させるパターンに設定し、この充放電サイクルを１サイクルとして、これを繰り返すことにより試験を行った。なお、図５に示す相対放電容量（％）は、下記の数１を用いて計算したものである。

【００４３】

【数１】相対放電容量（％）＝各サイクルにおける放電容量／初回放電容量

【００４４】（評価）図５から分かるように、本発明に係る実施例２の電池は、１００回のサイクル試験において、９１％の容量保持率を達成し、当該化合物が用いられていない比較例２よりも極めて優れたサイクル特性を発揮した。このように意図的に水分を加えた実施例において検証したことにより、本発明により開示された化合物が、重要な電池特性であるサイクル寿命において優れた効果を発揮することが明確に実証されたこととなる。

【００４５】 ここで、実施例２及び比較例２に係る電池は、捲回型電極体の場合と同じく、上記の方法により、電池ケース内に当該化合物を含ませて調整した種々の電池構成部材を用いて作製した。また、その他の部材、試験環境はすべての試料について同じとし、電池部材の乾燥は電池の組立直前まで十分に行い、電池の封止不良等による電池外部からの水分の浸入等の影響も排除した。

【００４６】 なお、エンジン起動用電池、電気自動車等のモータ駆動用電池においては、発進時や加速時、登坂時等に大電流の放電が必要とされ、このときには電池温度の上昇が起こる。しかし、本発明の化合物を添加した非水電解液等を用いた場合には、電池温度が上昇した場合であっても、捕獲されたＨＦが、再び遊離して非水電解液中に溶け込むことが起こりがたいために、サイクル特性良好な維持が図られる。

【００４７】 以上、本発明について、主に捲回型電極体を用いた場合を例に説明してきたが、本発明は電池構造を問うものでないことというまでもない。ここで、少容量のコイン電池では、電池自体が小さいために、その部品の作製、保管並びに電池組立を不活性ガス雰囲気で行

う等．水分管理が容易である。しかし．前述した捲回或いは積層型の内部電極体１・７を用いる容量の大きい電池の作製に当たっては、例えば、集電基板への電極活物質の塗工は比較的大規模な装置を用いる必要もあり、室内であっても外気と同様の雰囲気で行われ、特に水分管理を行う恒温恒湿室であっても完全に水分を除去した環境で作製されることは、製造コストの点から、現実的に考えがたい。

【００４８】 従って、本発明は、製造工程での水分管理が容易でない電池容量の大きな電池には好適に採用される。具体的には、捲回型或いは積層型の電極体１・７が用いられる電池容量が２Ａｈ以上のものに好適に採用される。電池の用途も限定されるものではないことはいうまでもないが．高出力．低内部抵抗と優れたサイクル特性が要求される車載用大容量電池として、エンジン起動用．又は電気自動車又はハイブリッド電気自動車のモータ駆動用に特に好適に用いることができる。

【００４９】

【発明の効果】 以上説明したように．本発明のリチウム二次電池によれば、当該化合物のルイス塩基性を示す＊

＊原子がＨＦを不活性化することにより．電池内の腐食及び悪質なＳＥＩ層の生成を抑制することから、電池反応の阻害を抑制することができる。この結果、本発明におけるリチウム二次電池は．特に高温におけるサイクル特性及び信頼性の向上が図られるという優れた効果を奏する。

【図面の簡単な説明】

【図１】 捲回型電極体の構造を示す斜視図である。

【図２】 積層型電極体の構造を示す斜視図である。

【図３】 サイクル試験における充放電パターンを示すグラフである。

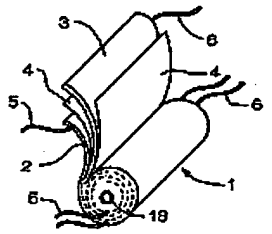
【図４】 実施例１のサイクル試験の結果を示すグラフである。

【図５】 実施例２のサイクル試験の結果を示すグラフである。

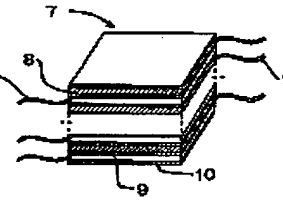
【符号の説明】

１…捲回型電極体、２…正極板、３…負極板、４…セパレータ、５…電極リード．６…電極リード、７…積層型電極体、８…正極板、９…負極板、１０…セパレータ、１１…電極リード、１２…電極リード．１３…巻芯。

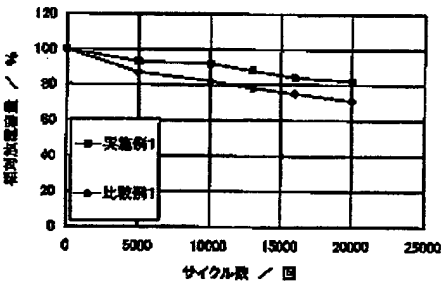
【図１】



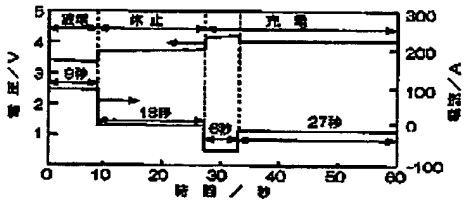
【図２】



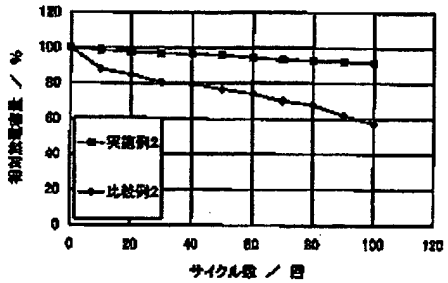
【図４】



【図３】



【図５】



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CB07 CB08 CB09 DA02 DA03
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* NOTICES *

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CLAIMS

[Claim(s)]

[Claim 1] The lithium secondary battery which is a lithium secondary battery using the nonaqueous electrolyte which is equipped with the electrode object which minds separator, and winds or comes to carry out the laminating of a positive-electrode board and the negative-electrode board, and contains a lithium compound as an electrolyte, and is characterized by the thing of the positive-electrode board concerned, the negative-electrode board concerned, the separator concerned, and the nonaqueous electrolyte concerned included for the 3-dimensional type siloxane compound in either at least.

[Claim 2] The lithium secondary battery according to claim 1 characterized by cell capacity being 2 or more Ahs.

[Claim 3] The lithium secondary battery according to claim 1 or 2 characterized by being a cell for mount.

[Claim 4] The lithium secondary battery according to claim 3 characterized by being used for an electric vehicle or a hybrid electric vehicle.

[Claim 5] The lithium secondary battery according to claim 3 characterized by being used for engine starting.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the lithium secondary battery excellent in a cycle property and reliability.
[0002]
[Description of the Prior Art] A lithium secondary battery is widely used increasingly in recent years as a rechargeable battery which bears the power supply of electronic equipment, such as carried type communication equipment and a note type personal computer, and in which charge and discharge with a big energy density are small and possible. Moreover, while the interest about saving-resources-izing or energy saving increases by making protection of international earth environment into a background, the lithium secondary battery is expected in the auto industry, respectively as the dc-battery for motorised for an electric vehicle or hybrid electric vehicles, and a deployment means of the power according [on the power industry and] to preservation of power night, and utilization of the mass lithium secondary battery suitable for these uses is made into pressing need.
[0003] Generally carbonaceous material [multiple oxide / lithium transition-metals], such as a hard carbon and a graphite, is used for a lithium secondary battery as a negative-electrode active material as a positive active material, respectively. Moreover, the reaction potential of the lithium secondary battery using such a material is as high as about 4.1 V, and, for this reason, cannot use drainage system nonaqueous electrolyte like the conventional rechargeable battery as nonaqueous electrolyte. then -- as the nonaqueous electrolyte of a lithium secondary battery -- an organic solvent -- a lithium ion (Li+) -- an electrolyte -- the nonaqueous electrolyte which dissolved the lithium compound is used
[0004]
[Problem(s) to be Solved by the Invention] It is a usual state that moisture is intermingled from the manufacture stage in the organic solvent used as the raw material of nonaqueous electrolyte here although it is a minute amount as contamination. Moreover, since various kinds of material and the parts which constitute a cell, for example, electrode active material powder, a current collection substrate (metallic foil) and a metal terminal, a cell case, etc. are generally saved in the usual air atmosphere, when the moisture which was sticking to the front face of these material or parts finishes creating a cell, it may enter into nonaqueous electrolyte.
[0005] When such moisture exists in nonaqueous electrolyte, an electrolyte decomposes with moisture, the danger that the acid, gas, etc. will occur becomes high, and it is a charge-and-discharge cycle property (the cell capacity change property by the repeat of charge and discharge is pointed out.) as a result. Hereafter, it is called a "cycle property". It deteriorates and the problem to which a battery life becomes short arises.
[0006] For example, although it is most observed as an electrolyte in order for a 6 fluoride [phosphoric-acid] lithium (LiPF6) to dissolve in an organic solvent and to show high electric conductivity, when LiPF6 is used, if moisture exists in an organic solvent, a hydrofluoric acid (HF)

will occur. This HF makes the metallic material of a cell container or a charge collector dissolve and corrode, and dissolves a positive active material, and makes transition metals eluted. Furthermore, the wicked SEI (Solid Electrolyte Interface) layer containing the metal is formed in a negative-electrode active material front face, it carries out checking an operation of Li+ etc., and the cause and bird clapper of cell degradation are known. Degradation of such a cell property appears notably in cycle operation which repeats charge and discharge, and serves as a critical defect of a rechargeable battery.

[0007] Then, by adding the straight chain-like polysiloxane compound which contained the silicone skeleton of (-Si-O-Si-) in the molecular structure in nonaqueous electrolyte and which is 1-dimensional structure, a current characteristic is raised, and improvement in a cycle property is achieved by JP,8-78053,A, and is carrying out the purport indication at it. However, by this method, since it is unstable in the electrolytic solution since an additive is a straight chain-like thing, and it is a macromolecule, dispersion will appear in the physical properties. And since a chain goes out from the thing of low molecular weight when the cell itself becomes an elevated temperature at the time of the use to which the lithium secondary battery in which this additive was included repeats the charge and discharge, the effect as an additive is lost and serves as a prevention object of a cell reaction conversely. Therefore, it is not suitable for the use of the electric vehicle which needs high performance in a cycle property high power nature and over a long period of time at all.
[0008]
[Means for Solving the Problem] the place which this invention is made in view of the trouble of the conventional technology mentioned above, and is made into the purpose -- the electrolytic solution and a cell -- by inactivating HF which will be contained in an electrode object or nonaqueous electrolyte as a result by making into a generating causative agent the moisture contained in the member etc., prevention of a cell reaction is suppressed and the lithium secondary battery excellent in a cycle property and reliability is offered -- it is in things
[0009] That is, according to this invention, it has the electrode object which minds separator, and winds or comes to carry out the laminating of a positive-electrode board and the negative-electrode board, and it is a lithium secondary battery using the nonaqueous electrolyte which contains a lithium compound as an electrolyte, and the positive-electrode board concerned, the negative-electrode board concerned, the separator concerned, and lithium secondary battery ** characterized by the thing of the nonaqueous electrolyte concerned included for the 3-dimensional type siloxane compound in either at least are offered.
[0010] In the lithium secondary battery of this invention, it is also desirable that electronic-conduction nature particles, such as acetylene black used as an electric conduction assistant, are distributed by the compound mentioned later. Without contributing such compound concerned to a cell reaction, by moreover adding an electric conduction assistant, elevation of internal resistance is suppressed and serves as an reaction inhibitor of good HF.
[0011] The lithium secondary battery of this invention is adopted suitable [cell capacity] for the large-sized cell of 2 or more Ahs. Moreover, it is suitably adopted as a cell for mount, and is suitably used as a power supply for motorised of the electric vehicle with which electric discharge of the power supply for engine starting which needs high power, and a high current is performed frequently, or a hybrid electric vehicle etc.
[0012]
[Embodiments of the Invention] The lithium secondary battery of this invention aims at improvement in a cycle property by suppressing prevention of the cell reaction by degradation of the nonaqueous electrolyte using the nonaqueous electrolyte which contains as an electrolyte the lithium compound which dissolves and produces a lithium ion (Li+). It cannot be overemphasized that this invention is not hereafter limited to the following operation gestalten although the operation gestalt of this invention is explained.
[0013] the lithium secondary battery of this invention -- the positive-electrode board 2, the negative-

electrode board 3, separator 4, and nonaqueous electrolyte -- a 3-dimensional type siloxane compound is made to be contained in either at least The nonaqueous electrolyte by which the compound concerned was added ["the compound concerned is contained" and] by sinking into the electrode board 2, and 3 and separator 4 here When the compound concerned beforehand applied to the case where the compound concerned will be contained in the electrode board 2-3 or separator 4, the electrode board 2-3, or separator 4 is filled up with nonaqueous electrolyte, it includes the case where will move into nonaqueous electrolyte and it will be contained also in nonaqueous electrolyte.
[0014] In the lithium secondary battery of this invention, as a method including this compound, even if there is little ** which is distributed by (2) separator front face distributed or covered by the front face of the electrode active material particle which constitutes (1) positive-electrode board and/or a negative-electrode board and by which carries out (3) detailed pulverization and suspension distribution is carried out into nonaqueous electrolyte, one of methods can be used. Therefore, it is also possible to use together two or more these meanses again.
[0015] As a method of including the compound concerned in the electrode board 2-3, specifically Even if it can mention the method of applying the compound concerned to the electrode board 2-3 using methods immersed in the compound agent concerned which melted the electrode board 2-3 to the meltable solvent, such as a method (dipping), a spray, and brush coating, and is the case where they are any The compound concerned is included, it dries behind and production of a subsequent electrode object is presented. It is also possible to carry out the detailed pulverization even to the grade which can use the method same also to making separator 4 front face distribute or fix, and does not carry out gravity settling of the compound concerned about the electrolytic solution, and to include the compound concerned uniformly.
[0016] Here, the method using what added the compound concerned beforehand is most suitably adopted as nonaqueous electrolyte. In this case, it is only that the addition mixture process of the compound concerned increases, and the assembly-operation process of a cell also has the advantage that work is also easy.
[0017] That is, what added the compound concerned is further used for the general nonaqueous electrolyte which comes to dissolve the electrolyte mentioned later in a predetermined organic solvent as the electrolytic solution with which it is filled up in a cell as an HF trap agent. It is possible to reduce HF concentration generated from the moisture in nonaqueous electrolyte before inserting an internal-electrode object in a cell by addition of the compound concerned. Moreover, after inserting an internal-electrode object in a cell, removal of HF generated from the moisture which was sticking to the electrode board etc. will be performed easily. By this, it contributes also to suppression of the metallic corrosion by HF etc., and suppression of wicked SEI generation, and it is thought that improvement in a cycle property is achieved.
[0018] now, as a 3-dimensional type siloxane compound which can be used for this invention concrete -- the 1-allyl compound -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [-- 9. -- 5. -- 1.13, 9.15, 15.17, and 13] OKUTA siloxane -- 1-(3-chloropropyl)-3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1-(4-vinyl phenyl)-3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, Ethyl -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, the 13] OKUTA siloxane-1-undecanone eight, 1, 3, 5, 7, 9, 11, and 14-heptacyclo HEKISHI tricyclo [7. 3.3.15, 11] HEPUTA siloxane - 3, 7, 14-triol, 1, 3, 5, 7, 9, 11, and 13-heptacyclo pentyl-15-[2-(diphenylphospino) ethyl] PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1, 3, 5, 7, 9, 11, and 13-heptacyclo pentyl-15-glycidyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 3, 5, 7, 9, 11, 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, a 13] OKUTA siloxane-1-butyronitrile, 3, 5, 7, 9, 11, 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane-1-oar, 3-(3, 5, 7, 9, 11, 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane-1-IRU) propyl methacrylate, 1, 3, 5, 7, 9, 11, and 14-heptacyclo pentyl tricyclo [7. 3.3.15, 11] HEPUTA siloxane-end - 3, 7, 14-triol, 1, 3, 5, 7,

9, 11, and 13-heptacyclo pentyl-15-vinyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, The 1-hydride -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, A methyl -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane-1-propionate, 1-[2-(5-norbornene-2-IRU) ethyl]-3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1, 3, 5, 7, 9, 11, 13, and 15-OKUTAKISU (dimethyl SHIRIROKISHI) PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1, 3, 5, 7, 9, 11, 13, and 15-OKUTABINIRUPENTA cyclo [9. 5.1.13, 9.15, 15.17, and 13] OKUTA siloxane are suitable. Since this has the cyclic structure, stably, it shows high Li+ conductivity to the electrolytic solution, and is suitably used for it as the compound concerned.

[0019] Here, in this invention, the mechanism in which a 3-dimensional type siloxane compound inactivates HF is explained. the time of assembling a cell, although the nonaqueous electrolyte which does not contain moisture was used for the electrolytic solution in this invention -- a cell -- since the moisture adhering to the member etc. cannot be removed completely, in the electrolytic solution, moisture will exist with a minute amount And the electrolytic solution decomposes with the moisture, the electrolytic solution and an electrolyte decompose, and HF, gas (CO2), etc. occur.

[0020] HF generated at this time dissolves a positive active material, makes transition metals eluted, and guides the wicked SEI generation containing the metal atom while it makes the metallic material of a cell container or a charge collector dissolve and corrode. In addition, a reaction will be promoted, so that the cell of the decomposition by electrolytic water is an elevated temperature, and the decomposition will progress. Since the generation reaction of SEI is exothermic reaction, decomposition by electrolytic water will be promoted by this heat, and HF will be generated further.

[0021] Then, in this invention, in the compound concerned, the atom in which Lewis-base nature is shown, i.e., O atom in which it has an unshared electron pair and electronic supply nature is shown, combines with HF which has an empty electron orbit in coordination, and it fixes HF in the molecular structure of the compound concerned. Thereby, HF in a cell is inactivated and it becomes possible to suppress the influence by HF. When the cell itself becomes an elevated temperature by this while a cell repeats charge and discharge, and the compound concerned fixes HF, generation of wicked SEI is suppressed.

[0022] Since especially the compound in this invention has the three-dimensional structure and has the cyclic structure of that it is the amount of macromolecules, and many, it can exist stably in the electrolytic solution also in an elevated temperature. Moreover, HF can be efficiently captured and fixed from there being many O atoms per unit volume in molecular structure. And 5 member ring structure which the compound concerned has is quite large, and does not prevent the movement from the ionic radius of Li+. Therefore, the 3-dimensional siloxane compound in this invention will demonstrate an effect certainly as an additive of the improvement in a cycle property in a lithium secondary battery.

[0023] In this invention, electronic-conduction nature particles, such as acetylene black, may be distributed by the compound concerned. By this, electric conductivity can be raised and elevation of internal resistance can be prevented.

[0024] Nonaqueous electrolyte using the lithium compound which dissolves and produces a lithium ion (Li+) as an electrolyte is used for the lithium secondary battery of this invention. Therefore, there is no limit in the other materials and cell structure in any way. Hereafter, it outlines about the primary member which constitutes a cell, and its structure.

[0025] One structure of the electrode object which can also be called core of a lithium secondary battery is the single cellular structure which sandwiched the separator which carried out press molding of positive/negative each electrode active material which is seen by the coin cell of small capacity disc-like.

[0026] One structure of the electrode object used for a cell with a large capacity to a small capacity cell like a coin cell is a wound type. As shown in the perspective diagram of drawing 1 , it winds

around the periphery of a winding core 13, and the wound type electrode object 1 is constituted so that the positive-electrode board 2 and the negative-electrode board 3 may not contact directly the positive-electrode board 2 and the negative-electrode board 3 through the separator 4 which consists of porous polymer. The number of the electrode leads 5-6 attached in the positive-electrode board 2 and the negative-electrode board 3 (it is hereafter described as "the electrode board 2 and 3".) can establish two or more electrode leads 5-6, and at least one can also make current collection resistance small what is necessary be just to be.

[0027] The laminating type which comes to carry out the laminating of the single cell type electrode object used for a coin cell to two or more steps as another structure of an electrode object is mentioned. As shown in drawing 2 , the laminating type electrode object 7 is what carried out the laminating of the positive-electrode board 8 and the negative-electrode board 9 of a predetermined configuration by turns on both sides of separator 10, and attaches the electrode lead 11-12 of at least one in one electrode board 8-9. The material of construction, the creation method, etc. of the electrode board 8-9 are the same as that of electrode board 2 and 3 grades in the wound type electrode object 1.

[0028] Next, the wound type electrode object 1 is explained to an example still in detail about the composition. The positive-electrode board 2 is produced by carrying out coating of the positive active material to both sides of a current collection substrate. Although a metallic foil with the corrosion resistance good as a current collection substrate over positive-electrode electrochemical reaction, such as an aluminum foil and a titanium foil, is used, a punching metal or a mesh (network) can also be used in addition to a foil. Moreover, as a positive active material, lithium transition-metals multiple oxides, such as a manganic acid lithium (LiMn 2O4), and a cobalt acid lithium (LiCoO2), a nickel acid lithium (LiNiO2), are used suitably, and carbon impalpable powders, such as acetylene black, are preferably added to these as an electric conduction assistant.

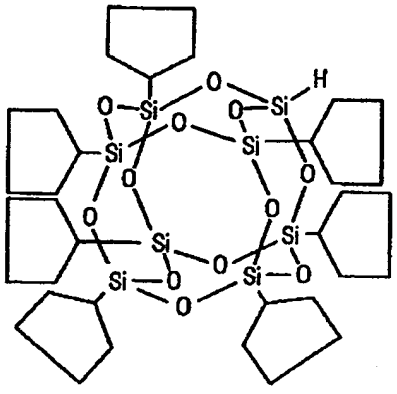
[0029] Coating of a positive active material is performed by using a roll coater etc., and applying and drying the slurry or paste which added and created the solvent, the binder, etc. to positive-active-material powder at a current collection substrate, and press processing etc. is performed if needed after that.

[0030] The negative-electrode board 3 can be created like the positive-electrode board 2. A metallic foil with the corrosion resistance good as a current collection substrate of the negative-electrode board 3 over negative-electrode electrochemical reaction, such as copper foil or a nickel foil, is used suitably. As a negative-electrode active material, nature powder of high graphitized carbon, such as amorphous system carbonaceous material and artificial graphites, such as soft carbon and a hard carbon, and a natural graphite, is used.

[0031] What made the polyethylene film (PE film) of Li+ permeability which has a micro pore three layer structures inserted with the porous polypropylene film (PP film) of Li+ permeability as separator 4 is used suitably. PE film becomes soft at about 130 degrees C, a micro pore is crushed, and this serves as the safe mechanism which suppresses, movement, i.e., the cell reaction, of Li+, when the temperature of an electrode object rises. And by pinching this PE film with PP film with a more high softening temperature, when PE film becomes soft, PP film holds a configuration, prevents contact and the short circuit of the positive-electrode board 2 and the negative-electrode board 3, and becomes securable [positive suppression of a cell reaction, and safety].

[0032] The electrode lead 5-6 is attached in the portion which the current collection substrate to which coating of the electrode active material is not carried out in the electrode board 2-3 at the time of the winding work of this electrode board 2-3 and separator 4 exposed, respectively. The thing of the shape of a foil which consists of the same quality of the material as the current collection substrate of each electrode board 2-3 as electrode lead 5-6 is used suitably. Installation to the electrode board 2-3 of the electrode lead 5-6 can be performed using ultrasonic welding, spot welding, etc. When the electrode lead 5-6 is attached, respectively at this time so that the electrode lead of one electrode may be arranged in the end side of the electrode object 1 as shown in drawing

1 , the contact during the electrode lead 5-6 can be prevented, and it is desirable.
[0033] Securing a flow with the electrode lead 5-6 with the terminal for taking out current outside first in the assembly of a cell, the produced electrode object 1 is inserted in a cell case, and it holds in a stable position. Then, after infiltrating nonaqueous electrolyte, a cell is produced by closing a cell case.
[0034] Next, the nonaqueous electrolyte used for the lithium secondary battery of this invention is explained. As a solvent, an independent solvent or mixed solvents, such as a thing of carbonate systems, such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and propylene carbonate (PC), and gamma-BUCHIRO lactin, a tetrahydrofuran, an acetonitrile, are used suitably.
[0035] As the lithium compound dissolved in such a solvent, i.e., an electrolyte, lithium complex fluorine compounds, such as a 6 fluoride [phosphoric-acid] lithium (LiPF6) and hoe lithium fluoride (LiBF4), or a lithium halogenide called a lithium perchlorate (LiClO4) is mentioned, and one kind or two kinds or more are dissolved and used for the aforementioned solvent. It is desirable for oxidative degradation to be unable to happen easily and to use conductive high LiPF6 of nonaqueous electrolyte especially.
[0036]
[Example] Hereafter, although this invention is explained still in detail based on an example, this invention is not limited to these examples.
(An example 1, example 1 of comparison) The cell concerning an example 1 and the example 1 of comparison Make 2OLiMn4 spinel into a positive active material, and to this acetylene black as an electric conduction assistant what was added about 4% of the weight by the outside ratio Furthermore, the positive-electrode board 2 which carried out coating and created the positive-electrode agent slurry which added and produced the solvent and the binder so that it might become the thickness of about 100 micrometers at both sides of an aluminum foil with a thickness of 20 micrometers, respectively, In addition to the same method as this, by making carbon powder into a negative-electrode active material, a wound type electrode object is produced using the created negative-electrode board 3 which carried out coating so that it may become the thickness of about 80 micrometers at both sides of copper foil with a thickness of 10 micrometers, respectively, and nonaqueous electrolyte is filled up with and produced after holding in a cell case. As nonaqueous electrolyte, LiPF6 as an electrolyte in the solution which dissolved so that it might become the concentration of 1 mol/l here at the amount mixed solvent of isochores of EC and DEC The 1-hydride -3 which is expressed with the following chemical formula (I) and which is the compound concerned, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, and the thing to which 0.1 mass % added 13] OKUTA siloxane by the outside ratio were used. All the cell capacity after first time charge of these various cells was about 10 Ah(s).
[0037]
[Formula 1]



(I)

[0038] Moreover, the cycle examination was performed by repeating this by making into 1 cycle the charge-and-discharge cycle shown in drawing 3 . That is, the cell of the charge state of 50% of depth of discharge was stopped for 18 seconds, after discharging for 9 seconds in current 100A equivalent to 10C (electric discharge rate), and it charged [70A] for 27 seconds by 18A continuously after charge for 6 seconds after that, and 1 cycle was set as the pattern again made into 50% of charge state. In addition, the gap of the depth of discharge in each cycle was stopped by tuning the 2nd current value (18A) of charge finely to the minimum. Moreover, in order to know change of the cell capacity under this durability test, volumetry set to charge halt voltage 4.1V and extinction voltage 2.5V by the current strength of 0.2C was performed suitably, and relative service capacity was calculated with the value which **(ed) cell capacity in the predetermined number of cycles by first-time cell capacity.
[0039] (Evaluation) In 20000 cycle examinations, the cell of the example 1 concerning this invention attained 82% of capacity retention, and demonstrated the cycle property better than the example 1 of comparison for which the compound concerned is not used so that drawing 4 might show. This is considered that the cycle life improved as a result of the compound concerned containing the atom in which Lewis-base nature is shown inactivating HF in the electrolytic solution.
[0040] Here, the cell concerning an example 1 and the example 1 of comparison was produced using the various cell composition members which were made to contain the compound concerned and adjusted it in the cell case by the above-mentioned method. moreover -- other members and the test atmosphere are the same about all samples -- carrying out -- a cell -- dryness of a member was fully performed just before the assembly of a cell, and the influence of permeation of the moisture from the cell outside by poor closure of a cell etc. was also eliminated
[0041] (An example 2, example 2 of comparison) The cell concerning an example 2 and the example 2 of comparison 2OLiMn4 spinel is made into a positive active material. to this electric conduction assistant slack acetylene black and a binder slack polyvinylidene fluoride by the weight ratio The positive-electrode board which made what was mixed by the ratio of 50:2:3 positive-electrode material, carried out press forming of the 0.02g of the positive-electrode material to disc-like [with a diameter / phi / of 20mm] by the pressure of 300 kg/cm2, and was produced, A coin cell type electrode object is produced using carbon as a negative-electrode board, and nonaqueous electrolyte is filled up with and produced after holding in a cell case. As nonaqueous electrolyte, about 1000 ppm (H2O) of moisture which causes cell property degradation at the amount mixed solvent of isochores of EC and DEC are added here. Moreover, the 1-hydride -3 which is the same compound as an example 1, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, About 500 ppm added and ** and the solution which dissolved LiPF6 as electrolytes so that it might become the concentration of 1 mol/l were used. All the cell capacity after first time charge of these various cells was about 1.3mA.
[0042] Next, the cycle examination in a coin cell type cell is explained. In this invention, the produced coin cell is responded to the capacity of a positive active material. Charge of total 3 hours is continuously performed on fixed voltage after charge until it is set to voltage 4.1V with 1.3mA of current of 1C. It was set as the pattern which similarly discharges with fixed current of 1.3mA of current of 1C, and is made to discharge until voltage is set to 2.5V, and examined by repeating this by making this charge-and-discharge cycle into 1 cycle. In addition, the relative service capacity (%) shown in drawing 5 is calculated using following several 1.
[0043]
[Equation 1] Service capacity / first time service capacity in relative service-capacity (%) = each cycle [0044] (Evaluation) In 100 cycle examinations, the cell of the example 2 concerning this invention attained 91% of capacity retention, and demonstrated the cycle property which was extremely superior to the example 2 of comparison for which the compound concerned is not used so that drawing 5 might show. Thus, it means that it was clearly proved by having verified in the

example which applied moisture intentionally that the effect which was excellent in the cycle life whose compound indicated by this invention is an important cell property was demonstrated.
[0045] Here, the cell concerning an example 2 and the example 2 of comparison was produced using the various cell composition members which were made to contain the compound concerned and adjusted it in the cell case by the above-mentioned method as well as the case of a wound type electrode object. moreover -- other members and the test atmosphere are the same about all samples -- carrying out -- a cell -- dryness of a member was fully performed just before the assembly of a cell, and the influence of permeation of the moisture from the cell outside by poor closure of a cell etc. was also eliminated
[0046] In addition, in cells for motorised, such as a cell for engine starting, and an electric vehicle, at the time of start and acceleration, electric discharge of a high current is needed at the time of a climb etc., and elevation of cell temperature takes place at this time. However, since it cannot happen easily that captured HF separates again and melts into nonaqueous electrolyte even if it is the case where cell temperature rises when the nonaqueous electrolyte which added the compound of this invention is used, maintenance with a good cycle property is achieved.
[0047] as mentioned above, although the case where a wound type electrode object is mainly used has been explained to an example about this invention, this invention is not what asks cell structure -- it is needless to say Here, moisture management is easy for inert gas atmosphere performing production of the part, storage, and cell assembly by the coin cell of few capacity, since the cell itself is small etc. However, in production of the cell with a large capacity using winding or the laminating type internal-electrode object 1-7 mentioned above For example, it is hard to consider being produced in the environment which removed moisture completely, even if it is the air conditioned room which the coating of the electrode active material to a current collection substrate needs to use comparatively large-scale equipment, is performed in the open air and the same atmosphere even if it is the interior of a room, and performs especially moisture management actually from the point of a manufacturing cost.
[0048] Therefore, this invention is suitably adopted as a cell with a big cell capacity for which the moisture management by the manufacturing process is not easy. Specifically, the cell capacity for which a wound type or the laminating type electrode object 1-7 is used is adopted suitable for the thing of 2 or more Ahs. Although it cannot be overemphasized that it is not that to which the use of a cell is also limited, it can use especially suitable for motorised [of the object for engine starting, an electric vehicle, or a hybrid electric vehicle] as a mass cell for mount by which high power, low internal resistance, and the outstanding cycle property are demanded.
[0049]
[Effect of the Invention] Since the corrosion in a cell and generation of a wicked SEI layer are suppressed according to the lithium secondary battery of this invention when the atom in which the Lewis-base nature of the compound concerned is shown inactivates HF as explained above, prevention of a cell reaction can be suppressed. Consequently, especially the lithium secondary battery in this invention does so the outstanding effect that improvement in a hot cycle property and reliability is achieved.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the lithium secondary battery excellent in a cycle property and reliability.

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PRIOR ART

[Description of the Prior Art] A lithium secondary battery is widely used increasingly in recent years as a rechargeable battery which bears the power supply of electronic equipment, such as carried type communication equipment and a note type personal computer, and in which charge and discharge with a big energy density are small and possible. Moreover, while the interest about saving-resources-izing or energy saving increases by making protection of international earth environment into a background, the lithium secondary battery is expected in the auto industry, respectively as the dc-battery for motorised for an electric vehicle or hybrid electric vehicles, and a deployment means of the power according [on the power industry and] to preservation of power night, and utilization of the mass lithium secondary battery suitable for these uses is made into pressing need.
[0003] Generally carbonaceous material [multiple oxide / lithium transition-metals], such as a hard carbon and a graphite, is used for a lithium secondary battery as a negative-electrode active material as a positive active material, respectively. Moreover, the reaction potential of the lithium secondary battery using such a material is as high as about 4.1 V, and, for this reason, cannot use drainage system nonaqueous electrolyte like the conventional rechargeable battery as nonaqueous electrolyte. then -- as the nonaqueous electrolyte of a lithium secondary battery -- an organic solvent -- a lithium ion (Li+) -- an electrolyte -- the nonaqueous electrolyte which dissolved the lithium compound is used

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EFFECT OF THE INVENTION

[Effect of the Invention] Since the corrosion in a cell and generation of a wicked SEI layer are suppressed according to the lithium secondary battery of this invention when the atom in which the Lewis-base nature of the compound concerned is shown inactivates HF as explained above, prevention of a cell reaction can be suppressed. Consequently, especially the lithium secondary battery in this invention does so the outstanding effect that improvement in a hot cycle property and reliability is achieved.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] It is a usual state that moisture is intermingled from the manufacture stage in the organic solvent used as the raw material of nonaqueous electrolyte here although it is a minute amount as contamination. Moreover, since various kinds of material and the parts which constitute a cell, for example, electrode active material powder, a current collection substrate (metallic foil) and a metal terminal, a cell case, etc. are generally saved in the usual air atmosphere, when the moisture which was sticking to the front face of these material or parts finishes creating a cell, it may enter into nonaqueous electrolyte.

[0005] When such moisture exists in nonaqueous electrolyte, an electrolyte decomposes with moisture, the danger that the acid matter, gas, etc. will occur becomes high, and it is a charge-and-discharge cycle property (the cell capacity change property by the repeat of charge and discharge is pointed out.) as a result. Hereafter, it is called a "cycle property". It deteriorates and the problem to which a battery life becomes short arises.

[0006] For example, although it is most observed as an electrolyte in order for a 6 fluoride [phosphoric-acid] lithium (LiPF6) to dissolve in an organic solvent and to show high electric conductivity, when LiPF6 is used, if moisture exists in an organic solvent, a hydrofluoric acid (HF) will occur. This HF makes the metallic material of a cell container or a charge collector dissolve and corrode, and dissolves a positive active material, and makes transition metals eluted. Furthermore, the wicked SEI (Solid Electrolyte Interface) layer containing the metal is formed in a negative-electrode active material front face, it carries out checking an operation of Li+ etc., and the cause and bird clapper of cell degradation are known. Degradation of such a cell property appears notably in cycle operation which repeats charge and discharge, and serves as a critical defect of a rechargeable battery.

[0007] Then, by adding the straight chain-like polysiloxane compound which contained the silicone frame of (-Si-O-Si-) in the molecular structure in nonaqueous electrolyte and which is 1-dimensional structure, a current characteristic is raised, and improvement in a cycle property is achieved by JP,8-78053,A, and is carrying out the purport indication at it. However, by this method, since it is unstable in the electrolytic solution since an additive is a straight chain-like thing, and it is a macromolecule, dispersion will appear in the physical properties. And since a chain goes out from the thing of low molecular weight when the cell itself becomes an elevated temperature at the time of the use to which the lithium secondary battery in which this additive was included repeats the charge and discharge, the effect as an additive is lost and serves as a prevention object of a cell reaction conversely. Therefore, it is not suitable for the use of the electric vehicle which needs high performance in a cycle property high power nature and over a long period of time at all.

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MEANS

[Means for Solving the Problem] the place which this invention is made in view of the trouble of the conventional technology mentioned above, and is made into the purpose -- the electrolytic solution and a cell -- by inactivating HF which will be contained in an electrode object or nonaqueous electrolyte as a result by making into a generating causative agent the moisture contained in the member etc., prevention of a cell reaction is suppressed and the lithium secondary battery excellent in a cycle property and reliability is offered -- it is in things

[0009] That is, according to this invention, it has the electrode object which minds separator, and winds or comes to carry out the laminating of a positive-electrode board and the negative-electrode board, and it is a lithium secondary battery using the nonaqueous electrolyte which contains a lithium compound as an electrolyte, and the positive-electrode board concerned, the negative-electrode board concerned, the separator concerned, and lithium secondary battery ** characterized by the thing of the nonaqueous electrolyte concerned included for the 3-dimensional type siloxane compound in either at least are offered.

[0010] In the lithium secondary battery of this invention, it is also desirable that electronic-conduction nature particles, such as acetylene black used as an electric conduction assistant, are distributed by the compound mentioned later. Without contributing such compound concerned to a cell reaction, by moreover adding an electric conduction assistant, elevation of internal resistance is suppressed and serves as an reaction inhibitor of good HF.

[0011] The lithium secondary battery of this invention is adopted suitable [cell capacity] for the large-sized cell of 2 or more Ahs. Moreover, it is suitably adopted as a cell for mount, and is suitably used as a power supply for motorised of the electric vehicle with which electric discharge of the power supply for engine starting which needs high power, and a high current is performed frequently, or a hybrid electric vehicle etc.

[0012]

[Embodiments of the Invention] The lithium secondary battery of this invention aims at improvement in a cycle property by suppressing prevention of the cell reaction by degradation of the nonaqueous electrolyte using the nonaqueous electrolyte which contains as an electrolyte the lithium compound which dissolves and produces a lithium ion (Li+). It cannot be overemphasized that this invention is not hereafter limited to the following operation gestalten although the operation gestalt of this invention is explained.

[0013] the lithium secondary battery of this invention -- the positive-electrode board 2, the negative-electrode board 3, separator 4, and nonaqueous electrolyte -- a 3-dimensional type siloxane compound is made to be contained in either at least The nonaqueous electrolyte by which the compound concerned was added ["the compound concerned is contained" and] by sinking into the electrode board 2, and 3 and separator 4 here When the compound concerned beforehand applied to the case where the compound concerned will be contained in the electrode board 2-3 or separator 4, the electrode board 2-3, or separator 4 is filled up with nonaqueous electrolyte, it includes the case where will move into nonaqueous electrolyte and it will be contained also in nonaqueous electrolyte.

[0014] In the lithium secondary battery of this invention, as a method including this compound, even if there is little ** which is distributed by (2) separator front face distributed or covered by the front face of the electrode active material particle which constitutes (1) positive-electrode board and/or a negative-electrode board and by which carries out (3) detailed pulverization and suspension

distribution is carried out into nonaqueous electrolyte, one of methods can be used. Therefore, it is also possible to use together two or more these meanses again.

[0015] As a method of including the compound concerned in the electrode board 2-3, specifically Even if it can mention the method of applying the compound concerned to the electrode board 2-3 using methods immersed in the compound agent concerned which melted the electrode board 2-3 to the meltable solvent, such as a method (dipping), a spray, and brush coating, and is the case where they are any The compound concerned is included, it dries behind and production of a subsequent electrode object is presented. It is also possible to carry out the detailed pulverization even to the grade which can use the method same also to making separator 4 front face distribute or fix, and does not carry out gravity settling of the compound concerned about the electrolytic solution, and to include the compound concerned uniformly.

[0016] Here, the method using what added the compound concerned beforehand is most suitably adopted as nonaqueous electrolyte. In this case, it is only that the addition mixture process of the compound concerned increases, and the assembly-operation process of a cell also has the advantage that work is also easy.

[0017] That is, what added the compound concerned is further used for the general nonaqueous electrolyte which comes to dissolve the electrolyte mentioned later in a predetermined organic solvent as the electrolytic solution with which it is filled up in a cell as an HF trap agent. It is possible to reduce HF concentration generated from the moisture in nonaqueous electrolyte before inserting an internal-electrode object in a cell by addition of the compound concerned. Moreover, after inserting an internal-electrode object in a cell, removal of HF generated from the moisture which was sticking to the electrode board etc. will be performed easily. By this, it contributes also to suppression of the metallic corrosion by HF etc., and suppression of wicked SEI generation, and it is thought that improvement in a cycle property is achieved.

[0018] now, as a 3-dimensional type siloxane compound which can be used for this invention concrete -- the 1-allyl compound -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [-- 9. -- 5. -- 1.13, 9.15, 15.17, and 13] OKUTA siloxane -- 1-(3-chloropropyl)-3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1-(4-vinyl phenyl)-3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, Ethyl -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, the 13] OKUTA siloxane-1-undecanone eight, 1, 3, 5, 7, 9, 11, and 14-heptacyclo HEKISHI tricyclo [7. 3.3.15, 11] HEPUTA siloxane - 3, 7, 14-triol, 1, 3, 5, 7, 9, 11, and 13-heptacyclo pentyl-15-[2-(diphenylphospino) ethyl] PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1, 3, 5, 7, 9, 11, and 13-heptacyclo pentyl-15-glycidyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 3, 5, 7, 9, 11, 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, a 13] OKUTA siloxane-1-butyronitrile, 3, 5, 7, 9, 11, 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane-1-oar, 3-(3, 5, 7, 9, 11, 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane-1-IRU) propyl methacrylate, 1, 3, 5, 7, 9, 11, and 14-heptacyclo pentyl tricyclo [7. 3.3.15, 11] HEPUTA siloxane-end - 3, 7, 14-triol, 1, 3, 5, 7, 9, 11, and 13-heptacyclo pentyl-15-vinyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, The 1-hydride -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, A methyl -3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane-1-propionate, 1-[2-(5-norbornene-2-IRU) ethyl]-3, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1, 3, 5, 7, 9, 11, 13, and 15-OKUTAKISU (dimethyl SHIRIROKISHI) PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, 1, 3, 5, 7, 9, 11, 13, and 15-OKUTABINIRUPENTA cyclo [9. 5.1.13, 9.15, 15.17, and 13] OKUTA siloxane are suitable. Since this has the cyclic structure, stably, it shows high Li+ conductivity to the electrolytic solution, and is suitably used for it as the compound concerned.

[0019] Here, in this invention, the mechanism in which a 3-dimensional type siloxane compound inactivates HF is explained. the time of assembling a cell, although the nonaqueous electrolyte which does not contain moisture was used for the electrolytic solution in this invention -- a cell -- since the moisture adhering to the member etc. cannot be removed completely, in the electrolytic solution,

moisture will exist with a minute amount And the electrolytic solution decomposes with the moisture, the electrolytic solution and an electrolyte decompose, and HF, gas (CO2), etc. occur.

[0020] HF generated at this time dissolves a positive active material, makes transition metals eluted, and guides the wicked SEI generation containing the metal atom while it makes the metallic material of a cell container or a charge collector dissolve and corrode. In addition, a reaction will be promoted, so that the cell of the decomposition by electrolytic water is an elevated temperature, and the decomposition will progress. Since the generation reaction of SEI is exothermic reaction, decomposition by electrolytic water will be promoted by this heat, and HF will be generated further.

[0021] Then, in this invention, in the compound concerned, the atom in which Lewis-base nature is shown, i.e., O atom in which it has an unshared electron pair and electronic supply nature is shown, combines with HF which has an empty electron orbit in coordination, and it fixes HF in the molecular structure of the compound concerned. Thereby, HF in a cell is inactivated and it becomes possible to suppress the influence by HF. When the cell itself becomes an elevated temperature by this while a cell repeats charge and discharge, and the compound concerned fixes HF, generation of wicked SEI is suppressed.

[0022] Since especially the compound in this invention has the three-dimensional structure and has the cyclic structure of that it is the amount of macromolecules, and many, it can exist stably in the electrolytic solution also in an elevated temperature. Moreover, HF can be efficiently captured and fixed from there being many O atoms per unit volume in molecular structure. And 5 member ring structure which the compound concerned has is quite large, and does not prevent the movement from the ionic radius of Li+. Therefore, the 3-dimensional siloxane compound in this invention will demonstrate an effect certainly as an additive of the improvement in a cycle property in a lithium secondary battery.

[0023] In this invention, electronic-conduction nature particles, such as acetylene black, may be distributed by the compound concerned. By this, electric conductivity can be raised and elevation of internal resistance can be prevented.

[0024] Nonaqueous electrolyte using the lithium compound which dissolves and produces a lithium ion (Li+) as an electrolyte is used for the lithium secondary battery of this invention. Therefore, there is no limit in the other materials and cell structure in any way. Hereafter, it outlines about the primary member which constitutes a cell, and its structure.

[0025] One structure of the electrode object which can also be called core of a lithium secondary battery is the single cellular structure which sandwiched the separator which carried out press molding of positive/negative each electrode active material which is seen by the coin cell of small capacity disc-like.

[0026] One structure of the electrode object used for a cell with a large capacity to a small capacity cell like a coin cell is a wound type. As shown in the perspective diagram of drawing 1 , it winds around the periphery of a winding core 13, and the wound type electrode object 1 is constituted so that the positive-electrode board 2 and the negative-electrode board 3 may not contact directly the positive-electrode board 2 and the negative-electrode board 3 through the separator 4 which consists of porous polymer. The number of the electrode leads 5-6 attached in the positive-electrode board 2 and the negative-electrode board 3 (it is hereafter described as "the electrode board 2 and 3".) can establish two or more electrode leads 5-6, and at least one can also make current collection resistance small what is necessary be just to be.

[0027] The laminating type which comes to carry out the laminating of the single cell type electrode object used for a coin cell to two or more steps as another structure of an electrode object is mentioned. As shown in drawing 2 , the laminating type electrode object 7 is what carried out the laminating of the positive-electrode board 8 and the negative-electrode board 9 of a predetermined configuration by turns on both sides of separator 10, and attaches the electrode lead 11-12 of at least one in one electrode board 8-9. The material of construction, the creation method, etc. of the electrode board 8-9 are the same as that of electrode board 2 and 3 grades in the wound type electrode object 1.

[0028] Next, the wound type electrode object 1 is explained to an example still in detail about the composition. The positive-electrode board 2 is produced by carrying out coating of the positive active

material to both sides of a current collection substrate. Although a metallic foil with the corrosion resistance good as a current collection substrate over positive-electrode electrochemical reaction, such as an aluminum foil and a titanium foil, is used, a punching metal or a mesh (network) can also be used in addition to a foil. Moreover, as a positive active material, lithium transition-metals multiple oxides, such as a manganic acid lithium (LiMn 2O4), and a cobalt acid lithium (LiCoO2), a nickel acid lithium (LiNiO2), are used suitably, and carbon impalpable powders, such as acetylene black, are preferably added to these as an electric conduction assistant.

[0029] Coating of a positive active material is performed by using a roll coater etc., and applying and drying the slurry or paste which added and created the solvent, the binder, etc. to positive-active-material powder at a current collection substrate, and press processing etc. is performed if needed after that.

[0030] The negative-electrode board 3 can be created like the positive-electrode board 2. A metallic foil with the corrosion resistance good as a current collection substrate of the negative-electrode board 3 over negative-electrode electrochemical reaction, such as copper foil or a nickel foil, is used suitably. As a negative-electrode active material, nature powder of high graphitized carbon, such as amorphous system carbonaceous material and artificial graphites, such as soft carbon and a hard carbon, and a natural graphite, is used.

[0031] What made the polyethylene film (PE film) of Li+ permeability which has a micro pore three layer structures inserted with the porous polypropylene film (PP film) of Li+ permeability as separator 4 is used suitably. PE film becomes soft at about 130 degrees C, a micro pore is crushed, and this serves as the safe mechanism which suppresses, movement, i.e., the cell reaction, of Li+, when the temperature of an electrode object rises. And by pinching this PE film with PP film with a more high softening temperature, when PE film becomes soft, PP film holds a configuration, prevents contact and the short circuit of the positive-electrode board 2 and the negative-electrode board 3, and becomes securable [positive suppression of a cell reaction, and safety].

[0032] The electrode lead 5-6 is attached in the portion which the current collection substrate to which coating of the electrode active material is not carried out in the electrode board 2-3 at the time of the winding work of this electrode board 2-3 and separator 4 exposed, respectively. The thing of the shape of a foil which consists of the same quality of the material as the current collection substrate of each electrode board 2-3 as electrode lead 5-6 is used suitably. Installation to the electrode board 2-3 of the electrode lead 5-6 can be performed using ultrasonic welding, spot welding, etc. When the electrode lead 5-6 is attached, respectively at this time so that the electrode lead of one electrode may be arranged in the end side of the electrode object 1 as shown in drawing 1 , the contact during the electrode lead 5-6 can be prevented, and it is desirable.

[0033] Securing a flow with the electrode lead 5-6 with the terminal for taking out current outside first in the assembly of a cell, the produced electrode object 1 is inserted in a cell case, and it holds in a stable position. Then, after infiltrating nonaqueous electrolyte, a cell is produced by closing a cell case.

[0034] Next, the nonaqueous electrolyte used for the lithium secondary battery of this invention is explained. As a solvent, an independent solvent or mixed solvents, such as a thing of carbonate systems, such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and propylene carbonate (PC), and gamma-BUCHIRO lactin, a tetrahydrofuran, an acetonitrile, are used suitably.

[0035] As the lithium compound dissolved in such a solvent, i.e., an electrolyte, lithium complex fluorine compounds, such as a 6 fluoride [phosphoric-acid] lithium (LiPF6) and hoe lithium fluoride (LiBF4), or a lithium halogenide called a lithium perchlorate (LiClO4) is mentioned, and one kind or two kinds or more are dissolved and used for the aforementioned solvent. It is desirable for oxidative degradation to be unable to happen easily and to use conductive high LiPF6 of nonaqueous electrolyte especially.

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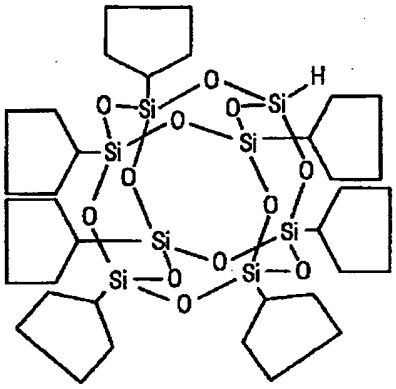
EXAMPLE

[Example] Hereafter, although this invention is explained still in detail based on an example, this invention is not limited to these examples.
(An example 1, example 1 of comparison) The cell concerning an example 1 and the example 1 of comparison Make 2OLiMn4 spinel into a positive active material, and to this acetylene black as an electric conduction assistant what was added about 4% of the weight by the outside ratio Furthermore, the positive-electrode board 2 which carried out coating and created the positive-electrode agent slurry which added and produced the solvent and the binder so that it might become the thickness of about 100 micrometers at both sides of an aluminum foil with a thickness of 20 micrometers, respectively, In addition to the same method as this, by making carbon powder into a negative-electrode active material, a wound type electrode object is produced using the created negative-electrode board 3 which carried out coating so that it may become the thickness of about 80 micrometers at both sides of copper foil with a thickness of 10 micrometers, respectively, and nonaqueous electrolyte is filled up with and produced after holding in a cell case. As nonaqueous electrolyte, LiPF6 as an electrolyte in the solution which dissolved so that it might become the concentration of 1 mol/l here at the amount mixed solvent of isochores of EC and DEC The 1-hydride -3 which is expressed with the following chemical formula (I) and which is the compound concerned, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, and the thing to which 0.1 mass % added 13] OKUTA siloxane by the outside ratio were used. All the cell capacity after first time charge of these various cells was about 10 Ah(s).
[0037]
[Formula 1]



(I)

[0038] Moreover, the cycle examination was performed by repeating this by making into 1 cycle the charge-and-discharge cycle shown in drawing 3 . That is, the cell of the charge state of 50% of depth of discharge was stopped for 18 seconds, after discharging for 9 seconds in current 100A equivalent to 10C (electric discharge rate), and it charged [70A] for 27 seconds by 18A continuously after charge for 6 seconds after that, and 1 cycle was set as the pattern again made into 50% of charge state. In addition, the gap of the depth of discharge in each cycle was stopped by tuning the 2nd current value (18A) of charge finely to the minimum. Moreover, in order to know change of the cell capacity under this durability test, volumetry set to charge halt voltage 4.1V and extinction voltage

2.5V by the current strength of 0.2C was performed suitably, and relative service capacity was calculated with the value which **(ed) cell capacity in the predetermined number of cycles by first-time cell capacity.

[0039] (Evaluation) In 20000 cycle examinations, the cell of the example 1 concerning this invention attained 82% of capacity retention, and demonstrated the cycle property better than the example 1 of comparison for which the compound concerned is not used so that drawing 4 might show. This is considered that the cycle life improved as a result of the compound concerned containing the atom in which Lewis-base nature is shown inactivating HF in the electrolytic solution.

[0040] Here, the cell concerning an example 1 and the example 1 of comparison was produced using the various cell composition members which were made to contain the compound concerned and adjusted it in the cell case by the above-mentioned method. moreover -- other members and the test atmosphere are the same about all samples -- carrying out -- a cell -- dryness of a member was fully performed just before the assembly of a cell, and the influence of permeation of the moisture from the cell outside by poor closure of a cell etc. was also eliminated

[0041] (An example 2, example 2 of comparison) The cell concerning an example 2 and the example 2 of comparison 2OLiMn4 spinel is made into a positive active material. to this electric conduction assistant slack acetylene black and a binder slack polyvinylidene fluoride by the weight ratio The positive-electrode board which made what was mixed by the ratio of 50:2:3 positive-electrode material, carried out press forming of the 0.02g of the positive-electrode material to disc-like [with a diameter / phi / of 20mm] by the pressure of 300 kg/cm2, and was produced, A coin cell type electrode object is produced using carbon as a negative-electrode board, and nonaqueous electrolyte is filled up with and produced after holding in a cell case. As nonaqueous electrolyte, about 1000 ppm (H2O) of moisture which causes cell property degradation at the amount mixed solvent of isochores of EC and DEC are added here. Moreover, the 1-hydride -3 which is the same compound as an example 1, 5, 7, 9, 11 and 13, and 15-heptacyclo pentyl PENTA cyclo [9. 5.1.13, 9.15, 15.17, 13] OKUTA siloxane, About 500 ppm added and ** and the solution which dissolved LiPF6 as electrolytes so that it might become the concentration of 1 mol/l were used. All the cell capacity after first time charge of these various cells was about 1.3mA.

[0042] Next, the cycle examination in a coin cell type cell is explained. In this invention, the produced coin cell is responded to the capacity of a positive active material. Charge of total 3 hours is continuously performed on fixed voltage after charge until it is set to voltage 4.1V with 1.3mA of current of 1C. It was set as the pattern which similarly discharges with fixed current of 1.3mA of current of 1C, and is made to discharge until voltage is set to 2.5V, and examined by repeating this by making this charge-and-discharge cycle into 1 cycle. In addition, the relative service capacity (%) shown in drawing 5 is calculated using following several 1.

[0043]

[Equation 1] Service capacity / first time service capacity in relative service-capacity (%) = each cycle [0044] (Evaluation) In 100 cycle examinations, the cell of the example 2 concerning this invention attained 91% of capacity retention, and demonstrated the cycle property which was extremely superior to the example 2 of comparison for which the compound concerned is not used so that drawing 5 might show. Thus, it means that it was clearly proved by having verified in the example which applied moisture intentionally that the effect which was excellent in the cycle life whose compound indicated by this invention is an important cell property was demonstrated.

[0045] Here, the cell concerning an example 2 and the example 2 of comparison was produced using the various cell composition members which were made to contain the compound concerned and adjusted it in the cell case by the above-mentioned method as well as the case of a wound type electrode object. moreover -- other members and the test atmosphere are the same about all samples -- carrying out -- a cell -- dryness of a member was fully performed just before the assembly of a cell, and the influence of permeation of the moisture from the cell outside by poor closure of a cell etc. was also eliminated

[0046] In addition, in cells for motorised, such as a cell for engine starting, and an electric vehicle, at the time of start and acceleration, electric discharge of a high current is needed at the time of a climb etc., and elevation of cell temperature takes place at this time. However, since it cannot happen easily

that captured HF separates again and melts into nonaqueous electrolyte even if it is the case where cell temperature rises when the nonaqueous electrolyte which added the compound of this invention is used, maintenance with a good cycle property is achieved.

[0047] as mentioned above, although the case where a wound type electrode object is mainly used has been explained to an example about this invention, this invention is not what asks cell structure -- it is needless to say Here, moisture management is easy for inert gas atmosphere performing production of the part, storage, and cell assembly by the coin cell of few capacity, since the cell itself is small etc. However, in production of the cell with a large capacity using winding or the laminating type internal-electrode object 1-7 mentioned above For example, it is hard to consider being produced in the environment which removed moisture completely, even if it is the air conditioned room which the coating of the electrode active material to a current collection substrate needs to use comparatively large-scale equipment, is performed in the open air and the same atmosphere even if it is the interior of a room, and performs especially moisture management actually from the point of a manufacturing cost.

[0048] Therefore, this invention is suitably adopted as a cell with a big cell capacity for which the moisture management by the manufacturing process is not easy. Specifically, the cell capacity for which a wound type or the laminating type electrode object 1-7 is used is adopted suitable for the thing of 2 or more Ahs. Although it cannot be overemphasized that it is not that to which the use of a cell is also limited, it can use especially suitable for motorised [of the object for engine starting, an electric vehicle, or a hybrid electric vehicle] as a mass cell for mount by which high power, low internal resistance, and the outstanding cycle property are demanded.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the perspective diagram showing the structure of a wound type electrode object.
[Drawing 2] It is the perspective diagram showing the structure of a laminating type electrode object.
[Drawing 3] It is the graph which shows the charge-and-discharge pattern in a cycle examination.
[Drawing 4] It is the graph which shows the result of a cycle examination of an example 1.
[Drawing 5] It is the graph which shows the result of a cycle examination of an example 2.
[Description of Notations]
1 [-- A negative-electrode board, 4 / -- Separator, 5 / -- An electrode lead, 6 / -- An electrode lead, 7 / -- A laminating type electrode object, 8 / -- A positive-electrode board, 9 / -- A negative-electrode board, 10 / -- Separator, 11 / -- An electrode lead, 12 / -- An electrode lead, 13 / -- Winding core.] -- A wound type electrode object, 2 -- A positive-electrode board, 3

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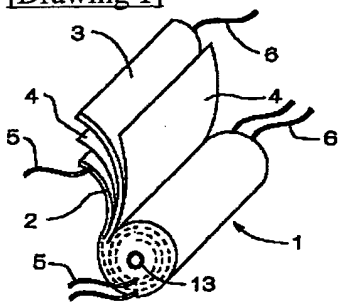
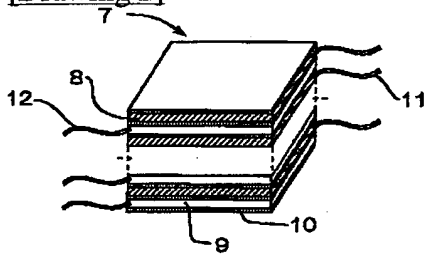
DRAWINGS

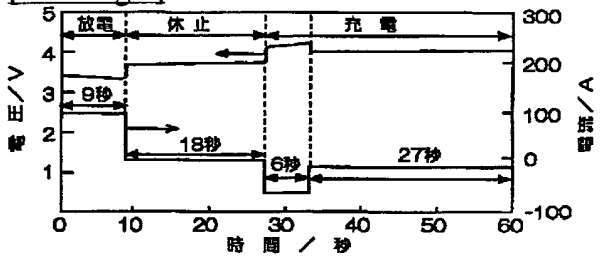
[Drawing 1]



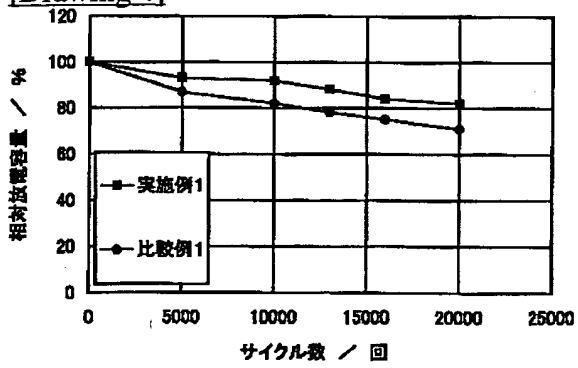
[Drawing 2]



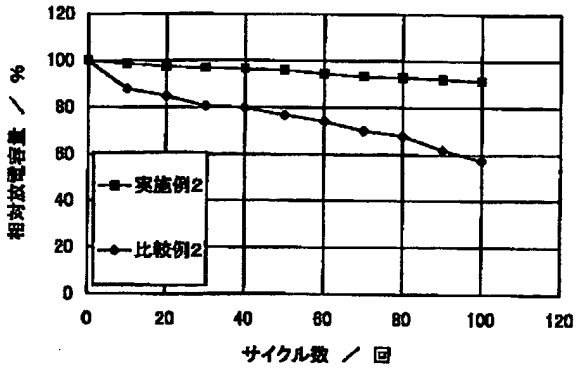
[Drawing 3]



[Drawing 4]



[Drawing 5]



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